

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.



⑯ Europäisches Patentamt
European Patent Office
Office européen des brevets



⑮ Publication number: 0 390 540 B1

⑯

EUROPEAN PATENT SPECIFICATION

⑯ Date of publication of patent specification: 03.08.94 ⑮ Int. Cl. 5: G02F 1/35, G02B 6/12, B05D 3/00, B05D 7/24
⑯ Application number: 90303320.7
⑯ Date of filing: 28.03.90

⑯ Process for preparing an organic compound thin film for an optical device.

⑯ Priority: 30.03.89 JP 80667/89

⑯ Date of publication of application:
03.10.90 Bulletin 90/40

⑯ Publication of the grant of the patent:
03.08.94 Bulletin 94/31

⑯ Designated Contracting States:
DE FR GB

⑯ References cited:
EP-A- 0 254 205
EP-A- 0 340 935

PATENT ABSTRACTS OF JAPAN, FILE SUP-
PLYER JAPS, Japanese Patent Office; & JP-
A-2 008 823

PATENT ABSTRACTS OF JAPAN, FILE SUP-
PLYER JAPS, Japanese Patent Office; & JP-
A-62 160 427

⑯ Proprietor: SHARP KABUSHIKI KAISHA
22-22 Nagalke-cho
Abeno-ku
Osaka 545(JP)

⑯ Inventor: Inoue, Atsuhisa
195-3, Kitsui,
Kashiba-cho
Kitakatsuragi-gun, Nara-ken(JP)
Inventor: Ishino, Mariko
Yanagimoto-haltsu, 645-2,
Oshikuma-cho
Nara-shi Nara-ken(JP)
Inventor: Akagi, Yoshiro
1-50-22, Hannan-cho
Abeno-ku, Osaka(JP)

⑯ Representative: West, Alan Harry et al
R.G.C. Jenkins & Co.
26 Caxton Street
London SW1H 0RJ (GB)

EP 0 390 540 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

The present invention relates to a process for preparing an organic compound thin film for an optical device. Particularly, the thin film of the invention can be used in a non-linear optical device, photoelectric device, optical integrated-circuit device, and the like.

Organic compounds are attracting considerable attention in the above applicable fields thereof in that they have suitable characteristics but also allow relatively unrestrained material design. However, to use organic compounds in a practical device in such fields, molecules of these organic compounds need to be oriented and crystallized.

LB technique (Langmuir-Blodgett's technique) is conventionally known as a preparing technique of an organic thin film having an orientation property. This technique is characterized in that organic molecules, each of which has a hydrophilic group at one side and a hydrophobic group at the other side, are developed on a water surface so as to form a monomolecular layer, and such a layer is accumulated one after another with its molecules "stood" on a suitable substrate. Usually, this technique can yield a thin film whose molecular axis is oriented perpendicular to the substrate.

However, the following restrictions exist in LB technique to have a well-controllable and well-oriented monomolecular thin film. First, an organic molecule to be used must be so designed and synthesized as to have a long-chain alkyl group as a skeleton where a hydrophilic group and a hydrophobic group are well balanced at one end and the other end thereof, respectively. Second, since this technique is a wet method, materials to be used and applications of the film are restricted. In addition, since a monomolecular layer is stacked one after another, it takes long time to form a thin film.

There is a vacuum vapor deposition technique other than LB technique to have an organic compound thin film. This technique is a dry method and widely used to form an organic compound thin film of a low to high molecular compound.

Generally, it is not always easy to control orientation of molecules in this technique. To overcome this problem, Japanese Unexamined Patent Publication SHO 160427/1987 discloses such a technique that a polyester orientation film which is uniaxially oriented is used as a substrate to control orientation of vapor-deposited organic molecules. This technique is characterized in that a high molecular film as a substrate is rendered uniaxially oriented by drawing or the like; and an organic compound is vapor-deposited thereon by vacuum vapor deposition. However, a thin film prepared by the technique does not have enough orientation

degree for practical use.

Thus, a thin film prepared by each of the above techniques does not have enough molecular orientation, therefore, it cannot exhibit enough non-linear optical effects such as a second harmonic and the like.

It is an object of the invention to provide a process for preparing an organic compound thin film wherein organic molecules or crystals thereof are highly oriented in vacuum vapor deposition technique, the organic compound thin film being useful in a non-linear optical device and the like.

The inventors of this invention have found that highly oriented crystals constituting a thin film are vapor-deposited when geometric linear streaks with a microscopic unevenness are formed on a substrate surface of amorphous organic polymer and an organic compound thin film is then vapor-deposited thereon. This is supposed that, by forming the geometric linear streaks with a microscopic unevenness, a portion of or the whole very top surface of the amorphous polymer substrate comes to have strong physical interaction with the deposited molecules.

Thus, according to the present invention, there is provided a process for preparing an organic compound thin film for use in an optical device comprising the steps of forming a multiplicity of geometric linear streaks with a microscopic unevenness on a surface of a substrate, at least said surface being made up of an amorphous organic polymer layer; thereafter vapor-depositing on said surface an organic compound capable of exhibiting non-linear optical characteristics to form an oriented non-linear optical material film.

Fig. 1 is an explanatory view showing a vapor deposition apparatus used in an example of the invention.

Figs. 2(a) to 2(c) are each an X-ray diffraction pattern of MNA thin films prepared in the example of the invention and comparative examples 1 and 2, respectively.

In the present invention, a multiplicity of geometric linear streaks with microscopic unevenness on a substrate at least whose surface is made up of an amorphous organic polymer layer are formed.

The above amorphous organic polymer can be selected from, for example, polyimides, phenolic resins, poly(methyl methacrylates), polystyrenes, and their low grade pre-polymers (usually their polymerization degree ranges from 10^3 to 10^5), and the like.

If functional groups in the principal chain or side chain of the amorphous organic polymer are appropriately selected, orientation of the deposited molecules (molecules of an organic compound capable of exhibiting non-linear optical characteristics) may become highly controllable because of

synergistic effects with the geometric linear streaks.

The amorphous organic polymer can be molded into a flat or curve plate of 0.01 to 10 μm thick to form a substrate by using a known method. Usually, it is more convenient to coat a plate or curve plate of an inorganic compound, for example, silicon, glass, or the like with an amorphous organic polymer by using a known method so as to form a substrate with an amorphous organic polymer layer.

The abovementioned geometric linear streaks allow the organic compound exhibiting non-linear optical characteristics to orient, and can be formed on the amorphous organic polymer layer constituting a surface of the above substrate.

A size of unevenness made by the geometric linear streaks is not specifically limited, but desirably as small as a size of the deposited molecule (dozens of \AA to hundreds of \AA). The size in section of unevenness may be 0.5 nm (5 \AA) to 1 μm , preferably 1 nm to 50 nm (10 \AA to 500 \AA) in gap and in pitch. However, it is difficult to obtain a well-oriented thin film if the size of unevenness is out of the above range.

The geometric linear streaks may be formed by mechanical rubbing, lithography using electromagnetic wave including light wave, charged-particle beam, neutral beam, chemical etching, or the like. Especially, rubbing with fine fibers is convenient and preferable.

In the present invention, the organic compound capable of exhibiting non-linear optical characteristics is vapor-deposited on the substrate to form the non-linear optical material layer. The organic compound capable of exhibiting non-linear optical characteristics can be selected from, for example, 2-methyl-4-nitroaniline, 7-diethylamino-4-methyl-cumarin, 3-nitroaniline, 5-nitouracil, α -resolcinol, 3-aminophenol, 1,3-dinitrobenzene, 2-bromo-4-nitroaniline, methyl 2-[(2,4-dinitrophenyl)amino]-propanoate, N,N'-dimethylurea, 3-methyl-4-nitropyridine -1-oxide, N-(4-nitrophenyl)-(L)-prolinol, and the like. Among them, 2-methyl-4-nitroaniline is preferable because it exhibits marked non-linear optical characteristics.

Conditions for carrying out the vapor deposition are not particularly limited. However, the deposited film thickness is preferably approximately 10 nm (100 \AA) to 10 μm to obtain a well-oriented non-linear optical material film. Additionally, too high temperature of the vapor source is not desirable to avoid decomposition of the organic compound.

According to the present invention, the geometric linear streaks cause the organic compound exhibiting non-linear optical characteristics to orient in a predetermined direction, the organic compound being vapor-deposited on the substrate. This makes it possible to remarkably enhance the ori-

entation property of the non-linear optical material layer which is formed on the organic compound exhibiting non-linear optical characteristics. As well, it becomes possible to form non-linear optical material layers different in physical and chemical properties by selecting a functional group in the amorphous polymer constituting the surface of the substrate.

10 Example 1

Here, a process for preparing a crystalline thin film of 2-methyl-4-nitroaniline (hereinafter abbreviated as MNA), which is attracting attention as an organic compound material exhibiting great non-linear optical effects, is exemplified to specifically describe the invention with reference to the drawings. It is to be noticed that materials used for the substrate and vapor deposition are not limited to polyimide and MNA, respectively.

Preparation of the MNA non-linear optical material layer is performed using a vacuum vapor deposition apparatus shown in Fig. 1. First, a solution of a polyamic acid in N-methylpyrrolidone was spin-coated on a quartz glass substrate. After drying, it was heated and baked (at 300 $^{\circ}\text{C}$) to form a polyimide film of approximately 1000 \AA thick. Further, the surface of the polyimide film was rubbed in the following manner to form geometric linear streaks. The obtained polyimide film was first pressed against a cloth with its fibers gigged under a predetermined pressure, the fiber being approximately 10 μm in diameter. The substrate was then moved at a constant speed in a fixed direction. Further, the substrate was washed with an organic solvent such as isopropyl alcohol or the like to yield the substrate 1. Unevenness in section of the geometric linear streaks was 1 - 50 nm (10 - 500 \AA) in gap and 1 - 50 nm (10 - 500 \AA) in pitch.

The substrate 1 was attached to a substrate holder 2 and a commercially available MNA reagent was put in a crucible 5. Subsequently, air in a glass bell jar 10 was discharged through a vent opening 12 to have a vacuum bell jar. Next, temperature of the substrate 1 was kept at 0 $^{\circ}\text{C}$, and the crucible 5 accommodating the MNA was heated under vacuum of the order of 10^{-6} Torr to sublimate the MNA, so that the MNA was vapor-deposited on the substrate 1 to form a thin film of approximately 3 μm thick.

Comparative Example 1

A MNA thin film was formed in the same manner as in the Example 1 with the exception that no polyimide film was formed on the quartz substrat .

Comparative Example 2

A MNA thin film was formed in the same manner as in the Example 1 with the exception that the rubbing and washing were not carried out.

Then, X-ray diffraction analysis was conducted on crystalline orientation of the MNA thin films prepared in Example 1 of the invention, and in Comparative Examples 1 and 2, respectively. Fig. 2(a) to 2(c) are each an X-ray diffraction pattern of the MNA films prepared in the Example 1 of the invention and Comparative Examples 1 and 2, respectively. According to the X-ray diffraction patterns, in the case of the MNA thin film [Fig. 2(b)] formed on the quartz substrate in Comparative Example 1, there appeared both strong reflections (112) and (020). As well, in the case of the MNA thin film [Fig. 2(c)] formed on the polyimide-film surface substrate in Comparative example 2, there appeared an extremely strong reflection (112) and a slight reflection (204).

In contrast, in the case of the MNA thin film prepared in Example 1 of the invention, the MNA thin film exhibited nearly complete uniaxial orientation in the (112) direction as shown in Fig. 2(a).

Accordingly, the above facts prove that the present invention is an excellent process for preparing an organic compound thin film (non-linear optical material layer). As well, the MNA thin film prepared on the quartz glass substrate via the polyimide film rubbed in accordance with the invention can be suitably used in a waveguide-type non-linear optical device.

Thus, according to the present invention, a non-linear optical material film having a very high orientation property can be prepared. Further, by using this non-linear optical material film, a high-quality non-linear optical device can be manufactured, if it is configured with, for example, laser beam projecting means, the non-linear optical material film, and outgoing light detecting means for detecting outgoing light from the film.

Claims

1. A process for preparing an organic compound thin film for use in an optical device comprising the steps of forming a multiplicity of geometric linear streaks with microscopic unevenness in cross-section on a surface of a substrate, at least said surface being made up of an amorphous organic polymer layer; thereafter vapor-depositing on said surface an organic compound capable of exhibiting non-linear optical characteristics to form an oriented non-linear optical material film.

2. A process for preparing an organic compound thin film as set forth in Claim 1, wherein said amorphous organic polymer layer is made of a polyimide, phenolic resin, poly(methyl methacrylate) or polystyrene.
3. A process for preparing an organic compound thin film as set forth in Claim 1, wherein said geometric linear streaks have unevenness in cross-section with 0.5 nm (5 Å)- to 1 μm-gap and 0.5 nm (5 Å)- to 1 μm- pitch.
4. A process for preparing an organic compound thin film as set forth in Claim 1, wherein said geometric linear streaks are formed by mechanical rubbing, lithography using a charged- or neutral-beam, or chemical etching using etchant.
5. A process for preparing an organic compound thin film as set forth in Claim 1, wherein said organic compound capable of exhibiting non-linear optical characteristics is 2-methyl-4-nitroaniline, 7-diethylamino-4-methylcumarin, 3-nitroaniline, 5-nitouracil, α-resolcinol, 3-aminophenol, 1,3-dinitrobenzene, 2-bromo-4-nitroaniline, methyl 2-[(2,4-dinitrophenyl)-amino]-propanoate, N,N-dimethylurea, 3-methyl-4-nitropyridine-1-oxide or N-(4-nitrophenyl)-(L)-prolinol.
6. A process for preparing an organic compound thin film as set forth in Claim 1, wherein said non-linear optical material film has a thickness of 10 nm (100 Å) to 10 μm.

Patentansprüche

1. Verfahren zum Herstellen eines dünnen Films aus organischem Material für die Verwendung in einer optischen Vorrichtung, umfassend die Stufen: Bilden einer Vielzahl geometrischer linearer Streifen von mikroskopischer Unebenheit im Querschnitt auf einer Oberfläche eines Substrats, wobei mindestens die Oberfläche aus einer amorphen organischen Polymereschicht hergestellt ist, anschliessendes Dampfabscheiden einer organischen Verbindung, welche sich dazu eignet, nicht-lineare optische Eigenschaften auszuüben, auf der Oberfläche, wobei ein orientierter, nicht-linearer, optischer Materialfilm gebildet wird.
2. Verfahren zum Herstellen eines dünnen Films aus organischem Material nach Anspruch 1, wobei die amorphe organische Polymerschicht aus Polyimid, Phenolharz, Poly(methylmethacrylat) oder Polystyrol hergestellt

wird.

3. Verfahren zum Herstellen eines dünnen Films aus organischem Material nach Anspruch 1, wobei die geometrischen linearen Streifen eine Unebenheit im Querschnitt von 0,5 nm (5 Å) bis 1 µm in bezug auf die Lücke und von 0,5 nm (5 Å) bis 1 µm in bezug auf den Teilungsabstand aufweisen.

4. Verfahren zum Herstellen eines dünnen Films aus organischem Material nach Anspruch 1, wobei die geometrischen linearen Streifen durch mechanisches Reiben, Lithographie unter Verwendung eines geladenen oder neutralen Strahls oder chemisches Ätzen unter Verwendung eines Ätzmittels gebildet werden.

5. Verfahren zum Herstellen eines dünnen Films aus organischem Material nach Anspruch 1, wobei das organische Material, das sich dazu eignet, nichtlineare optische Eigenschaften auszuüben, 2-Methyl-4-nitroanilin, 7-Diethylamino-4-methylcumarin, 3-Nitroanilin, 5-Nitouracil, α -Resorcin, 3-Aminophenol, 1,3-Dinitrobenzol, 2-Brom-4-nitroanilin, Methyl-2-[(2,4-dinitrophenyl)amino]propanoat, N,N'-Dimethylharnstoff, 3-Methyl-4-nitropyridin-1-oxid oder N-(4-Nitrophenyl)-(L)-prolinol ist.

6. Verfahren zum Herstellen eines dünnen Films aus organischem Material nach Anspruch 1, wobei der nicht-lineare optische Materialfilm eine Dicke von 10 nm (100 Å) bis 10 µm aufweist.

3. Procédé de préparation d'un film mince de composé organique selon la revendication 1, dans lequel lesdites stries linéaires géométriques présentent une inégalité en coupe transversale avec un intervalle de 0,5 nm (5 angstroms) à 1 µm et un pas de 0,5 nm (5 angstroms) à 1 µm.

4. Procédé de préparation d'un film mince de composé organique selon la revendication 1, dans lequel lesdites stries linéaires géométriques sont formées par frottement mécanique, lithographie utilisant un faisceau chargé ou neutre, ou par gravure chimique utilisant un agent de gravure.

5. Procédé de préparation d'un film mince de composé organique selon la revendication 1, dans lequel ledit composé organique susceptible de présenter des caractéristiques optiques non linéaires est la 2-méthyl-4-nitroaniline, la 7-diéthylamino-4-méthylcumarine, la 3-nitroaniline, le 5-nitouracile, l'alpha-résorcinol, le 3-aminophénol, le 1,3-dinitrobenzène, la 2-bromo-4-nitroaniline, le 2-[(2,4-dinitrophényl)-amino]-propanoate de méthyle, la N,N'-diméthylurée, le 3-méthyl-4-nitropyridine-1-oxyde ou le N-(4-nitrophényl)-(L)-prolinol.

6. Procédé de préparation d'un film mince de composé organique selon la revendication 1, dans lequel ledit film de matière optique non linéaire a une épaisseur de 10 nm (100 angstroms) à 10 µm.

35

40

45

50

55

FIG. 1

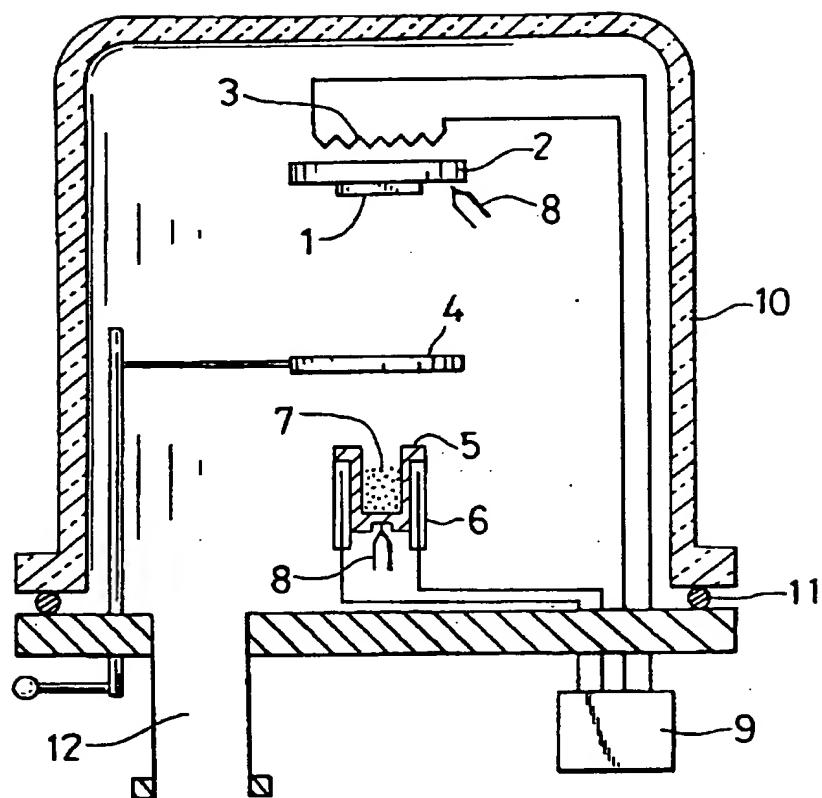
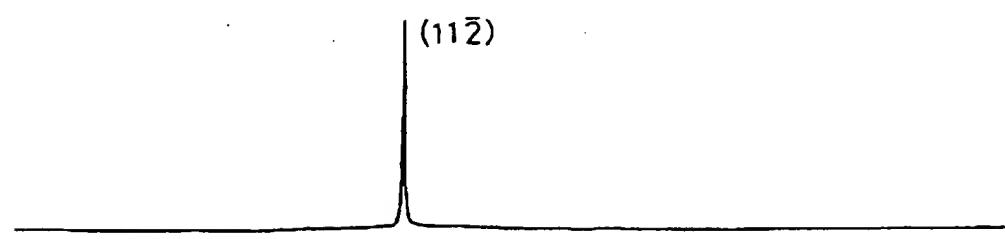
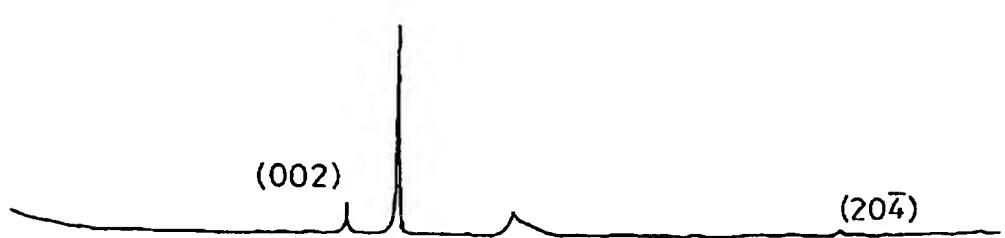


FIG. 2

(a)



(b)



(c)

